RATES OF PYROLYSIS AND COMBUSTION OF BARK BY THERMOGRAVIMETRIC ANALYSIS

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Wood supplies approximately 3 percent of the U.S. energy consumption (Schreuder and Tillman, 1980). Bark represents about 10-15% of the weight of the trunk cut in the forest. Wood combustion phenomena has been extensively reviewed (e.g., Tillman *et al.*, 1981). Recent technological development is reflected in an article by Barsin *et al.* (1988), and a report published by the Electric Power Research Institute (Johnston *et al.*, 1993). Fundamental understanding of wood pyrolysis has also grown substantially in the last two decades. Shafizadeh (1982) reviewed the wood pyrolysis and combustion kinetics based on weight loss profiles. About the same time, Hajaligol *et al.* (1982) reported the kinetics of the individual product species for rapid pyrolysis of cellulose. Boroson *et al.* (1989) observed that heterogeneous cracking of wood pyrolysis tars takes place over flesh wood char surface. Pyrolysis kinetics of different lignocellulosic materials have been investigated by Bilbao *et al.* (1989, 1990). Heat and mass transfer limitations are inevitable during burning of large particles, and have been the target of a number of modeling efforts (e.g., Kanury, 1972; Maa and Bailie, 1973; Chan *et al.*, 1985; Ragland *et al.*, 1988; Bilbao *et al.*, 1993).

Due to its lower physical strength and less uniform structure than interior wood, bark is usually burned along with wood waste as a fuel, particularly by sawmills and pulp mills. Bark has the heating value of 8,000 to 10,000 Btu/lb, which is higher than that of wood (Wegner, 1991). The objective of this paper is to experimentally acquire information about the bark kinetics during pyrolysis and combustion conditions. A kinetic model is also developed for the comparison.

EXPERIMENTAL

Since weight loss is used as a measure of bark conversion in the present study, the design of experiments has some salient features of a thermal balance, Figure 1. The center piece of the reactor is a cylindrical sample basket of dimension 1 in × 2 in length, which is made of 40 mesh stainless steel screen. The reactor vessel is an alumina tube with inside diameter of 2.5 in, which is heated to the desired temperature by a Thermcraft furnace model 23-18-1ZH with dimensions 3 in × 18 in long. The reactor is equipped with a distributor at about 6 in from the bottom end of the furnace, and a fluidized sand bed serving as a heat source of the gas stream.

Samples of pine bark, cut into 10mm spheres, were dried at 105°C for 24 hours before the experiment. Nitrogen and air were used as the fluidizing gas during pyrolysis and combustion, respectively. To begin a run, the sample basket containing a single particle of bark is lowering into the preheated fluidized sand bed. After a predetermined period of time, the basket was raised to a water-jacketed, reversed-nitrogen flow section for rapid quenching. Sample weight before and after the experiment were recorded. The ultimate analysis of the bark sample is shown in Table 1.

Experiments were conducted at sand temperatures 750, 800 and 850°C for pyrolysis; and 500, 600, 700 and 800°C for combustion. To achieve these temperatures, the furnace was set 90°C higher than the desired sand temperature. The gas flowrate, 15,000 ml/min, was chosen to ensure that it was three times higher than the theoretical air required at highest burning rate.

KINETIC MODEL

The bark combustion model under consideration contains three major components: bark pyrolysis, char combustion, and heat transfer.

During pyrolysis, the organic portion of the bark converts to volatiles and solid char, i.e.,

$$Bark + heat \rightarrow \underset{(V)}{Volatiles} + \underset{(1-V)}{Char} \tag{1}$$

Here, the fraction of weight loss, V, is used as an index of bark conversion. The volatile compounds include the gaseous species and tarry species disengaged from the char. Similar to a number of coal pyrolysis studies (e.g., Howard, 1981), bark pyrolysis is treated as a first order reaction in the following form

$$\frac{dV}{dt} = k_1(V_\infty - V) \tag{2}$$

where V_∞ is the final volatile yield as time approaches infinity. The pyrolysis rate constant k_1 is assumed to follow the Arrhenius law

$$k_1 = k_{10} e^{-\frac{E_1}{RT_p}} \tag{3}$$

where T_p is particle temperature, and E_1 is the pyrolysis activation energy.

Similar to coal pyrolysis (Howard, 1988), we observed temperature dependence of V_∞ during regression. Niksa (1988) proposed that phase equilibrium determines partitioning of tar in the gas and condensed phase, and the final volatile yield in the gas phase, V_∞, depends on temperature as follows:

$$V_\infty(T_p) = V_{10}e^{-\frac{E_3}{T_p}} \tag{4}$$

where V_{10} and E_3 are adjustable parameters.

In the presence of oxygen, oxidation of the organics in the char contributes to additional weight loss

$$\underset{(W)}{Char} + O_2 \rightarrow CO_2 + H_2O \tag{5}$$

Assuming char combustion is first order with respect to oxygen concentration and the weight of char, we obtain

$$\frac{dW}{dt} = -k_1(V_\infty - V) - k_2' W(O_2) \tag{6}$$

Since oxygen was continuously fed into the combustor at a rate four times that required for burning the volatile carbon, oxygen concentration is assumed to be constant during the combustion. Thus, we can combine k_2' and the oxygen concentration as a new constant k_2 and Eq. 6 becomes

$$\frac{dW}{dt} = -k_1(V_\infty - V) - k_2 W \tag{7}$$

Assuming that the combustion rate constant, k_2, follows the Arrhenius law,

$$k_2 = k_{20}e^{-\frac{E_2}{RT_p}} \tag{8}$$

Mass transfer limitations, such as oxygen diffusion into the char, are usually involved in combustion of particles of 1 cm in diameter, thus the rate measured based on Eqs. 7 and 8 should be considered effective or global reaction rate (Carberry, 1976).

Combustion of volatiles generated in bark pyrolysis will also take place outside bark particles at the same time,

$$Volatiles + O_2 \rightarrow H_2O + CO_2 \tag{9}$$

However, since this reaction does not contribute to the weight loss and it is not included in the present model.

Weight loss measurements indicate that devolatilization of bark particles takes place almost instantaneously at 800°C. However, at 500°C, devolatilization does not start until at about 20 s. These observations imply that heat transfer is a limiting factor in the range of our investigation, and an equation governing the temperature variation of the particle is required. Based on the published value of thermal conductivity of cellulosic materials, 0.12 $W.m^{-1}.K^{-1}$ (Reed, 1983), the estimated Nusselt number of heat transfer for a bark particle gives values in the range 0.8 to 1.8. Since this is not a large number, we assume that the temperature is uniform inside a bark particle during pyrolysis and combustion. It should be mentioned that there is evidently a radial temperature profile and diffusion limitations of volatiles inside the wood particles with diameter 56 mm (Bilbao *et al.*, 1993). Energy balance yields

$$\rho_p V_p C_p \frac{dT_p}{dt} = Ah(T-T_p) + \varepsilon A\sigma(T_w^4 - T_p^4) + \Delta H_p r_p W_{p0} + \Delta H_o r_o W_{p0} \tag{10}$$

Equation 10 states that temperature rise of a bark particle is governed by convective heat transfer, radiative heat transfer, heat of pyrolysis, and heat of combustion. We assume that the heat of volatiles combustion is carried away by gas, and is not included in this equation. Our calculation reveals that convection contributes to less than 20% of radiative heat transfer. Furthermore, experiments indicate that char combustion is much slower than pyrolysis, and char combustion does not contribute significant weight loss and temperature rise during the heat-up period. Thus, the first and the fourth terms on the right hand side of Eq. 10 are eliminated in the regression process, i.e.,

$$\rho_p V_p C_p \frac{dT_p}{dt} = \varepsilon A \sigma (T_w^4 - T_p^4) + \Delta H_p r_p W_{p0} \qquad (11)$$

Again, due to the fact that significant char combustion does not take place during the heat-up period, the bark particle external surface area, A, in Eq. 11 is assumed to be a constant during the combustion process. The published value for heat capacity of bark, C_p, is 0.327cal/g.°C (Reed, 1983), and the nominal density of bark particle, ρ_p, was experimentally determined, 0.42kg/dm^3.

The model discussed above has three dynamic equations, Eqs. 2, 7 and 11. Equations 3, 4 and 8 are also required for the integration of the three dynamic equations. The seven parameters, k_{10}, E_1, k_{20}, E_2, V_{10}, E_3 and ΔH_p are recovered from regression through comparison of the model with the data obtained from pyrolysis and combustion experiments. The optimization has been achieved by resorting to BCONF/DBCONF, a subroutine in the International Mathematical and Statistical Library which minimizes a multi-variable function subject to bounds on the variables using a quasi-Newton method and a finite-difference gradient. The integration of the large sets of differential equations has been carried out on a Cray X-MP2/216 supercomputer with LSODE, a software package based on Gear's method for solving stiff differential equations (Hindmarsh, 1982).

RESULTS AND DISCUSSION

The optimization procedure resulted in the following values of the seven system parameters:

$k_{10} = 1{,}557\ s^{-1}$ $\quad E_1 = 37{,}333$ J/mol

$k_{20} = 0.295\ s^{-1}$ $\quad E_2 = 22{,}028$ J/mol

$V_{10} = 0.862$ $\quad E_3 = 228$ K

$\Delta H_p = 434$ J/g of dry bark

The value of final volatile yield, V_{10}, is in good accord with the reported volatile matter for cedar bark, 0.869, moisture and ash free basis (Tillman *et al.*, 1981). The heat of pyrolysis, ΔH_p, is somewhat higher than that reported for cellulose, 274 J/g (Bilbao *et al.*, 1993), and that for cottonwood, 268 J/g (Pan, 1993). This discrepancy may be caused by the high heating rate, or the assumptions used in the present study. It has been demonstrated that high temperatures favor decomposition to volatiles, which require heat, while low temperatures favor char formation, which release heat (Shafizadeh and DeGroot, 1976). Bilbao *et al.* and Pan obtained their values through DSC analysis with a heating rate below 20 °C/min, and the heating rate in the present study is above 400°C/min. The activation energy of bark pyrolysis is consistent with those found by other researchers: 24,208 J/mol between 290 and 400°C (Bilbao *et al.*, 1993) and 52,900 J/mol above 325°C for pine wood (Bilbao *et al.*, 1991).

The experimental data in general are in good accord with the predictions of the model. Only part of our results are presented below. Figures 2 presents the comparisons of pyrolysis and combustion results from experiments at the sand temperatures 800°C. The predicted temperature profiles of bark particle during heating are also included in this Figure. Slower rise in temperature between 170 to 230°C indicates endothermic reaction of pyrolysis in this temperature range, which is somewhat narrower than that reported by Wegner, 100 to 450°C (1991). Note that char combustion does not contribute significant weight loss in the first 20s, while pyrolysis is essentially complete during this time. This observation is consistent with the assumption that heat of combustion of char does not play an important role during the heat-up period.

Figures 3 demonstrates the weight loss profiles during combustion at 600°C sand temperature. The data generally conform well with the model predictions. However, at 500°C, the pyrolysis is slower in the experiment than predicted by the model. This illustrates the limitations of the present phenomenological model. Bark is a complex material and its decomposition products contain numerous compounds, while the present model uses weight loss as an index of reaction conversion. The assumptions associated with heat transfer can also cause discrepancies. Furthermore, from thermodynamic principles and collision theory, both the frequency factor and the activation energy can be functions of temperature (Zellner, 1984).

Fragmentation of bark particles and volatiles ignition during combustion may be important to the future developments of phenomenological model. We observed fragmentation of bark particles at temperatures 600°C and above. Each bark particle breaks into 2 to 6 pieces along its geological planes after 15 to 25 seconds in the furnace, and higher temperatures cause more vigorous fragmentation. Fragmentation results in increase in larger surface areas and therefore reduced transfer limitations. Furnace temperature also affects ignition of volatiles. At 800 and 700°C, flame starts at about 2 s after the bark particle is lowered into the furnace. At 600°C, flame was observed at about 5s. At 500°C, ignition was delayed to 19s.

CONCLUSIONS

Bark from pine has been investigated in both pyrolysis and combustion environments. The experimental data are in good accord with a kinetic model which includes three dynamic equations: bark pyrolysis, char combustion, and heat transfer to the bark particle. Three of the seven parameters, final volatile yield, heat of pyrolysis, and activation energy of bark pyrolysis, are in good agreement with published values for similar species. These results suggest that the model is capable of depicting the weight loss profiles in a furnace with a temperature in the range 500 to 850 °C.

Experiments also reveal that volatiles evolution and char combustion take place during two different periods of time during the thermal process. Furthermore, fragmentation of bark particles was also observed at temperatures above 600°C.

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TABLE 1. Ultimate Analysis of Bark (Report by Huffman Laboratory)

dry-loss, %	4.92
ash, %	4.08
carbon, %	51.20
hydrogen, %	5.66
oxygen, %	40.67
nitrogen, %	0.21
sulphur, %	0.02

The sample was ground prior to analysis. Moisture was determined by loss on drying in air at 105°C to a constant weight and is on an as received basis. All other results are on a dried sample basis by weight.

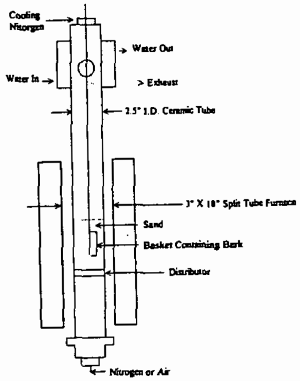

Figure 1. Experimental apparatus

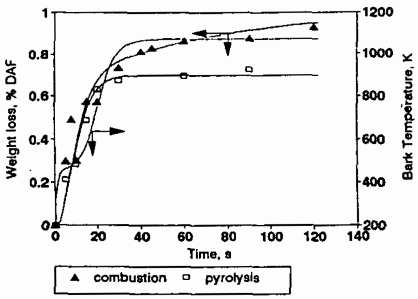

Figure 2. Experimentally observed and model predicted weight loss of bark during pyrolysis at 800°C sand temperature. Predicted bark particle temperature is also shown.

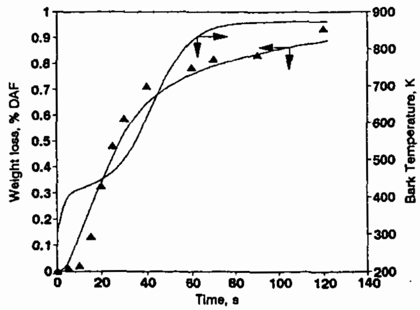

Figure 3. Experimentally observed and model predicted weight loss of bark during combustion at 600°C wall temperature. Predicted bark particle temperature is also shown.